REF in SERIAL NO. 066,851 L

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AN 98-124765 [12] WPIDS
DNN N98-099284 DNC C98-041193
TI Lead-free pewter alloy - includes predetermined amount of **silver** , **copper** , **germanium** and **tin**.
DC M23 P55
PA (NIHA-N) NIPPON HANDA KK
CYC 1
PI JP 10006075 A 980113 (9812)* 5 pp B23K035-26 <--
ADT JP 10006075 A JP 96-174210 960613
PRAI JP 96-174210 960613
IC ICM **B23K035-26**
ICS **C22C013-00**
AB JP10006075 A UPAB: 980323
The alloy includes 1-6 wt.% of **silver**, 0.05-3 wt.% of **copper**, 0.03-2 wt.% of **germanium** and remaining wt.% of **tin**.

0.5- 4 wt.% of **bismuth** may also be added, to improve 'wetness' (sic).

ADVANTAGE - Simplifies manufacturing processes. Reduces fusion temperature. Prevents generation of lift off phenomenon of function part of through hole component with lead. Offers alloy with good reversibility. Improves wetness property. Reduces surface tension during fusion. Improves soldering property and soldering intensity.

Laid-Open Number: 10-6075
Laid-Open Date: January 13, 1998
Application Number: 8-174210
Application Date: June 13, 1996
Int. Class Number: B23K 35/26: C22C 13/00
Applicant: Nippon Solder Co., Ltd.

[Title of the Invention] Lead-Free Solder Alloy

[Abstract]

[Object] To provide a lead-free solder alloy resisting any lift-off phenomenon, and having high plasticity and good wetting property.

[Summary] The lead-free solder alloy of this invention comprises 1.0 to 6.0% by weight of Ag, 0.05 to 3.0% by weight of Cu and 0.03 to 2.0% by weight of Ge, the balance being Sn. More particularly, it is an Sn-Ag-Cu-Ge quaternary alloy having an Sn:Ag ratio of 99.0:1.0 to 94.0:6.0 and a Cu:Ge ratio of 60:40, and resisting any lift-off phenomenon. As it contains Cu, it is high in plasticity, and easy to work mechanically. The addition of 0.5 to 4.0% by weight of Bi to the lead-free solder alloy improves its wetting property, solderability and solder strength.

[What Is Claimed Is]

[Claim 1] A lead-free solder alloy comprising 1.0 to 6.0% by weight of Ag, 0.05 to 3.0% by weight of Cu and 0.03 to 2.0% by weight of Ge, the balance being Sn.

[Claim 2] An alloy as set forth in claim 1, wherein Sn and Ag have a ratio of 99.0:1.0 to 94.0:6.0, and Cu and Ge have a ratio of 60:40.

[Claim 3] An alloy as set forth in claim 1 or 2, further containing 0.5 to 4.0% by weight of Bi.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a lead-free solder alloy.

[0002]

[Prior Art] Soldering has a long history as a bonding method, and eutectic solder comprising 63% by weight of Sn and 37% by weight of Pb is widely used as a solder alloy.

[0003] The interest in environmental problems which has recently been increasing on a worldwide basis has called attention to the toxicity of the lead which solder contains. In the United States, this problem has been taken up so seriously that there is a movement toward the legal restriction of the use of lead. The same situation exists in Europe, too, and the change to lead-free solder alloys is going to be a worldwide trend.

[0004] A great deal of research work has been done about lead-free solder in accordance with the changes in social circumstances, and a number of lead-free solder alloys are now commercially available. The commercially available lead-free solder alloys are generally of the Sn-Ag, Sn-Bi, Sn-Zn or Sn-In type, and all contain Sn as their principal component, and Bi, In or other substitutes for Pb. Small amounts of other elements are added to those lead-free solder alloys to improve their properties in which they are inferior to the conventional Sn-Pb solder alloy, but there is no alloy that has come to be widely used as a substitute for the Sn-Pb solder alloy.

[0005] The relevant prior art literature includes JP7-40079A and JP7-32188A.

[0006]

[Problems to Be Solved by the Invention] The following is a statement of the problems pointed out in connection with the presently available lead-free solder alloys:

(1) The melting and reflow temperatures are so high that it is necessary to change the existing production facilities, or the heat-resisting design for the electronic parts to be mounted;

(2) The alloy containing a large amount of Bi has so wide a melting temperature range that during its solidification, the joint formed thereby on any through-hole part, or part with a lead undergoes a lift-off due to a difference in solidifying

time from one portion thereof to another;

(3) They are too low in plasticity for any working, such as rolling, after casting; and

(4) They are low in wetting property, solderability and solder strength.

[0007] It is an object of this invention to provide a lead-free solder alloy resisting any lift-off phenomenon, and having high plasticity and good wetting property.

[0008]

[Means for Solving the Problems] The lead-free solder alloy of this invention comprises 1.0 to 6.0% by weight of Ag, 0.05 to 3.0% by weight of Cu and 0.03 to 2.0% by weight of Ge, the balance being Sn. It may further contain 0.5 to 4.0% by weight of Bi.

[0009]

[Modes of Embodying the Invention] A lead-free solder alloy embodying this invention is a quaternary alloy of Sn, Ag, Cu and Ge produced by adding an alloy consisting of 60% by weight of Cu and 40% by weight of Ge to an alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag. The alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag is a eutectic alloy of Sn and Ag which has conventionally been used as lead-free high-temperature solder. The alloy consisting of 98.0% by weight of Sn and 2.0% by weight of Ag has its Ag content lowered

to the extent not affecting its properties substantially, and is less expensive. Either of these alloys and a eutectic alloy of Cu and Ge consisting of 60% by weight of Cu and 40% by weight of Ge were mixed in the ratio of 1000:1 to 100:5 to form alloys embodying this invention.

[0010] Moreover, 0.5 to 4.0% by weight of Bi was added to an alloy produced by mixing the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag and the alloy consisting of 60% by weight of Cu and 40% by weight of Ge in the ratio of 100:1.

[0011] The alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag is a conventional lead-free high-temperature solder alloy considered as one of good substitutes for the Sn-Pb solder alloy, but since it has a melting point as high as, say, 221°C and is low in wetting property and mechanical workability after casting, it is not used as it is, but various elements are added to it to form Sn-Ag lead-free solder alloys.

[0012] Lead-free solder alloys embodying this invention were also prepared by adding a plurality of elements to the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag.

[0013] Ge forms with Sn and Ag a tertiary eutectic alloy having a melting point which is lower than that of the Sn-Ag alloy.

[0014] The addition of Cu makes it possible to form an alloy

having finely divided crystal grains, and thereby improved levels of plasticity and mechanical workability after casting. Cu and Ge have a ratio of 60:40 to form a eutectic alloy, so that any elevation of the melting point by Cu may be minimized.

[0015] Thus, the Sn-Ag-Cu-Ge quaternary alloy was produced by adding the alloy consisting of 60% by weight of Cu and 40% by weight of Ge to the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag.

[0016] The alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag and the alloy consisting of 60% by weight of Cu and 40% by weight of Ge are employed in a ratio of, say, 100 : up to 5 (giving up to 2.0% by weight of Ge), and no further addition of the Cu-Ge alloy brings about any lower melting temperature.

[0017] The addition of Bi brings about a lower melting temperature. Moreover, Bi brings about a lower surface tension, and thereby improved wetting and spreading property. Bi is, however, brittle, and the addition of too much Bi gives a brittle alloy of low plasticity. The alloy containing a large amount of Bi has a solidus temperature in the vicinity of 139°C, the eutectic point of the Sn-Bi alloy, and thereby so wide a melting temperature range that during its solidification, the joint formed thereby on any through-hole part, or part with a lead may undergo a lift-off due to a difference in solidifying time

from one portion thereof to another, as stated before. Thus, the range of Bi has an upper limit of 4.0% by weight.

[0018] Although the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or 98.0% by weight of Sn and 2.0% by weight of Ag was employed for producing the alloys embodying this invention as described above, any Sn-Ag alloy of different composition can also be employed for producing the lead-free solder alloy of this invention if it has an Sn:Ag ratio of 99.0:1.0 to 94.0:6.0.

[0019]

[Examples] The liquidus and solidus temperatures of each of samples having alloy compositions as shown in Table 1 were determined by differential thermal analysis, and are shown in Table 1.

[0020]

[Table 1]

Alloy composition (wt.%)	Liquidus temperature (°C)	Solidus temperature (°C)
Sn 96.5 Ag 3.5	221.0	221.0
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 0.1	220.2	216.6
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 0.25	219.9	216.6
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 0.5	218.3	215.3
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 1.0	215.9	215.3
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 2.0	214.4	214.4
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 5.0	214.4	214.4
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 1.0•Bi 1	215.4	212.1
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 1.0•Bi 2	214.5	210.6
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 1.0•Bi 3	213.9	208.5
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 1.0•Bi 4	212.4	206.7
(Sn 96.5 Ag 3.5) 100:(Cu 60 Ge 40) 1.0•Bi 5	211.5	206.1

[0021] As is obvious from Table 1, the addition of the alloy consisting of 60% by weight of Cu and 40% by weight of Ge to the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag lowers its liquidus temperature by about 5°C, and further addition of Bi lowers its liquidus temperature to nearly 210°C. These temperatures are comparable to those of e.g. ALLOY•H (Sn90 Bi7.5 Ag2 Cu0.5), the lead-free solder alloy proposed by The International Tin Research Institute of England, and indicate that the alloys are satisfactory for practical use as compared with the known lead-free solder alloys.

[0022] The alloys have a solidus temperature above 200°C, and are unlikely to cause any lift-off that would result from a wide melting temperature range.

[0023] Rolling tests were conducted on samples having alloy compositions as shown in Table 2 to compare them in mechanical workability after casting, and the results including the presence of any ear cracking are shown in Table 2. The test was conducted by melting each sample at a temperature of 450°C, casting it into a cylinder having a diameter of 80 mm, forming it into a tape having a thickness of 3.0 mm and a width of 32 mm through a hydraulic extruder and rolling it to reduce its thickness stepwise from 3.0 mm to 0.05 mm.

[0024]

[Table 2]

Alloy composition (wt.%)	Results
Sn 96.5 Ag 3.5	Rolling to 0.05 mm was possible without any ear cracking
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0	Rolling to 0.05 mm was possible without any ear cracking
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 1	Rolling to 0.05 mm was possible without any ear cracking
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 2	Rolling to 0.05 mm was possible without any ear cracking
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 3	Rolling to 0.05 mm was possible without any ear cracking
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 4	Ear cracking occurred upon rolling to 0.1 mm
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 5	Ear cracking occurred upon rolling to 0.34 mm
ALLOY•H (Sn 90 Bi 7.5 Ag 2 Cu 0.5)	Ear cracking occurred upon rolling to 1.0 mm
H63S (Sn 63 Pb 37)	Rolling to 0.05 mm was possible without any ear cracking

[0025] The test results confirm that the lead-free solder alloy of this invention is high in plasticity, and high in mechanical workability after casting. The lead-free solder alloy of this invention could be rolled down to 0.05 mm without any ear cracking, though the rolling of ALLOY•H to 1.0 mm caused heavy ear cracking disabling any further rolling. The alloy containing Bi to the extent not exceeding 3.0% by weight could be rolled down to 0.05 mm without presenting any problem. The alloy containing 4.0% by weight of Bi showed ear cracking upon rolling to 0.1 mm, and the alloy containing 5% by weight of Bi showed ear cracking upon rolling to 0.34 mm. Thus, 4.0% by weight is a practically acceptable upper limit to the range of Bi.

[0026] Table 3 shows the results of a spreading test. The test was conducted by placing about 30 mg of each sample on a copper plate coated with a flux of the RA type and heating it for 30 seconds at a temperature 50°C higher than its liquidus

temperature to spread it on the copper plate. After cooling, the height of solder was measured by a micrometer, and its spreading ratio was calculated in accordance with JIS-Z3197. The results confirm that the lead-free solder alloy of this invention has a spreading ratio about 1 point higher than that of the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag.

[0027]

[Table 3]

Alloy composition (wt.%)	Spreading ratio	Melting temperature
Sn 96.5 Ag 3.5	74.7%	270°C
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0	75.5%	260°C
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 1	75.2%	260°C
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 2	75.1%	260°C
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 3	75.5%	260°C
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 4	75.7%	260°C
(Sn 96.5 Ag 3.5) 100 : (Cu 60 Ge 40) 1.0+Bi 5	77.0%	260°C
ALLOY•H (Sn 90 Bi 7.5 Ag 2 Cu 0.5)	77.4%	260°C
H63S (Sn 63 Pb 37)	91.4%	230°C

[0028] Although no specific test results have been shown for any alloy produced by adding the alloy consisting of 60% by weight of Cu and 40% by weight of Ge to the alloy consisting of 98.0% by weight of Sn and 2.0% by weight of Ag, or for any alloy further containing Bi, it is obvious that substantially the same results can be obtained as those attained by the alloy produced by adding the alloy consisting of 60% by weight of Cu and 40% by weight of Ge to the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag, or the alloy further containing

Bi. It is also easy to assume that any alloy produced by using any Sn-Ag alloy having an Sn:Ag ratio of 99.0:1.0 to 94.0:6.0 gives substantially the same test results as those given by the alloy based on the alloy consisting of 96.5% by weight of Sn and 3.5% by weight of Ag.

[0029]

[Advantages of the Invention] As is obvious from the foregoing, the lead-free solder alloy of this invention, which is an Sn-Ag-Cu-Ge quaternary alloy, has so narrow a melting temperature range as to resist any lift-off of the joint formed on any through-hole part, or part with a lead.

[0030] As it contains Cu, the alloy is so high in plasticity as to facilitate any mechanical working, such as rolling, after casting.

[0031] Moreover, the presence of Bi lowers the surface tension of the molten alloy, and improves its wetting property, solderability and solder strength.